PRODUCTION OF BIODIESEL FROM PALM OIL THROUGH HETEROGENEOUS CATALYSIS USING CALCINED EGGSHELL

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NOMENCLATURE

B100	Pure biodiesel
B.E.T	Brunauer-Emmet-Teller
B.J.H.	Barrett, Joyner, Halenda
FAME	Free fatty acid methyl ester
FFA	Free fatty acid
FTIR	Fourier Transform Infrared Spectroscopy
GC	Gas chromatography
Ppm	part per million
XRD	X-Rat diffraction

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ABSTRACT

In recent years, shortage of fossil fuel, increasing price of crude oil and environmental issues have led to the scientific and research study in alternative fuel. Biodiesel is one of the alternate biofuels, due to its comparable fuel properties and cleaner emission to environment. In this study, transesterification of refined palm oil with methanol catalyzed by heterogeneous catalyst, calcined eggshell was studied and the suitable kinetic model was identified. Calcined eggshell was prepared by washing the fresh eggshell with boiling water and followed by calcinations of fresh eggshell at 900 ^{0}C. The calcined eggshells were characterized by X-ray *Diffraction* (XRD),Physisorption analysis (B.E.T.) method, andFourier transforms infrared spectroscopy (FTIR). Through the analysis, the calcined eggshell was found that identical to the commercial Calcium Oxide. Transesterification was studied at different parameter such as temperature (45^{0}C-65^{0}C), agitation intensity (200 rpm-500 rpm), catalyst weight percent (1.5%-6%), and methanol to oil weight ratio (12:1-6:1). The highest yield is 72.03% of Fatty Acid Methyl Ester (FAME). The kinetic data was fit to the kinetic model developed using first order model. It is found that the calcined eggshell is a potential catalyst which is comparable to other commercial catalyst.

PENGHASILAN BIODIESEL DARI MINYAK SAWIT MELALUI PENGMANGKINAN HETEROGEN DENGAN MENGGUNAKAN KULIT TELUR TERBAKAR

ABSTRAK

Kebelakang ini, kekurangan minyak, kenaikan harga minyak mentah dan isu-isu terhadap alam sekitar mendorongkan pangajian saintifik dan penyelidikan untuk mendapat bahan bakar alternatif. Biodiesel sebagai salah satu biofuel yang standing dengan sifat-sifat bahan bakar yang sedia-ada serta pelepasan gas-gas yang lebih bersih. Dalam kajian ini, pengtransesteran minyak sawit tertapis dengan pemangkin yang berbentuk pepejal. Pemangkin yang digunakan adalah kulit telur terbakar telah dikaji dan model yang sesuai untuk system tindak bala selah dikajikan.Kulit telur terbakar telah disediakan dengan menggunakan telur kulit segar yang telah dibersihkan dengan air panas dan seterusnya pembakaran atau pengkalsinan kulit telur ke 900 darjah Celsius dalamudaraselama 3 jam. Pemangkin atau kulit telur terbakar yang telah disediakan kemudiannya dicirikan dengan menggunakan pembelauan sinar-X (*XRD*), spektrometer Fourier Transform infra merah (*FT-IR*) dan pengukuran luas permukaan Brunner-Emmett-Teller (*BET*).Dalam pengajian yang telah buat, kulit telur terbakar ini mempunyai ciri-ciri yang sama dengan Calcium Oksida. Selain itu, pengtransesteran minyak sawit kepada hasil dikaji pada pembolehuba htindak balas seperti nisbah molar metanol/minyak(12:1-6:1), jumlah berat pemangkin (1.5%-6%) yang digunakan, suhu tindak balas(45^0C- 65^0C), dan intensiti pergolakan(200 rpm -500 rpm). Hasil diperoleh adalah 72.03 % biodiesel di bawah keadaan tindak balas optimum. Tindak balas adalah sepadan kepada model yang dicipta, model tesebut adalah pseudo-homo first order. Sebagai kesimpulan, kulit telur terbakar adalah berpotensi dimana ianya adalah setanding dengan pemangkin yang sedia ada dalam pasaran.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Majority energy consumption worldwide came from fossil sources (petroleum, coal and natural gas) and shortage is predicted in coming 50 years. Therefore finding an alternative energy is crucial. Renewable energy such as biodiesel is important fuel in future. Biodiesel is a green fuel that can be used in standard diesel engine and also in pure form known as B100. (Benjamin, 2007)

Biodiesel refers as Fatty Acid Methy Ester (FAME) also known as mono alkyl ester. It is produced using 4 different methods using in the market. The methods are catalysis (transesterification), pyrolysis, direct bending and Micro-emulsion. Amongst the 4 methods, transesterification was chosen since it increases the cetane number and has higher combustion efficiency. The present research focuses on transesterification aid with catalyst. Transesterification process uses vegetable oil and animal fat as the raw materials by reacting with an alcohol (methanol).

Vegetable oil and animal fat are organic triglyceride, which are the main source of producing biodiesel. Selection types of catalyst are depending on the content of FFA (free fatty acid) and water in the triglyceride. FFA will reduce the biodiesel yield during transesterification catalysed by using alkali catalyst due to soap formation (Endalew, 2011). In order to reduce the content of FFA, pre-treatment such as esterification with strong acid such as H_2SO_4 with alcohol is used to form ester(Sharma, 2008). In this study, refined palm oil will negligible amount of FFA will be used.

As mentioned, transesterification required catalyst to operate at ambient condition. 3 main categories of catalysts in the market are homogeneous, heterogeneous, and enzymatic. Homogeneous catalyst is in liquid form. Sodium Hydroxide and potassium hydroxide concentrated solution and the common catalyst used in producing biodiesel. Helwani, (2009) discussed that alkali catalyst is preferred since it is faster than acidic catalyst by 4000 times and stainless steel reactor couldn't resist the corrosion action from strong and concentrated acid. Nevertheless, the use of homogeneous catalyst has caused great impact to environment and market value of glycerine. Separation of the homogeneous catalyst from glycerine is time. Studies on heterogeneous catalyst are important and it can overcome the drawback. Heterogeneous catalyst such as, Calcium Oxide, Iron Sulfate, Fe_2SO_4 can be separated by filtration from mixture of glycerine. Lipases also are used as enzyme in enzymatic transesterification. It shows good result in selectivity. However it required longer reaction time than base catalyzed system. (Sharma, 2008)

1.2 Problem statements

1. In market, the common catalyst such as NaOH, and KOH are expensive and high cost in recovery of glycerine. In order to recover the FAME, washing process is used. However, washing process will generate much waste water. It is another environmental problem. In addition, the catalyst such as sodium hydroxide is used in industries and not environmental friendly, the recovery of glycerol after the reaction is impossible.
2. In the view of waste to wealth, eggshell containing high percentages of Calcium carbonate and can be transformed into calcium oxide, a strong earth alkaline metal oxide, which can be used to catalysed the transesterification of vegetable oil for biodiesel production. This can be done via calcinations process. The treated eggshell catalyst is comparable with commercial catalyst and it wouldn't cause any environment impact.

1.3 Research Objectives

1. To characterize calcined eggshell using X-ray Diffraction method (XRD), Fourier Transform Infrared (FTIR) and Physisorption analysis.
2. To study the effect of important parameters to the reaction.

3. To develop the suitable kinetic model.

1.4 Scope of the study

1. To characterize the calcined eggshell using FTIR, XRD and physisorption analysis.
2. To study the effect of important parameter such as temperature, agitation intensity, oil/methanol molar ratio and catalyst loading.
3. The fit the experimental data with the kinetic model such Pseudo-homo geneous model, Eley-Rideal model or Langmuir Hinshelwood model.

1.5 Significant of the study

Most of the vehicle still consuming petrol-diesel and it is one of the largest sources contributing to the greenhouse gases. The petro-diesel in future will be replaced by bio-fuel such as biodiesel. Biodiesel is environmental friendly by closed-carbon-cycle. This study is to generate more environment friendly catalysts to enhance the quantity and quality of the production of biodiesel.

Direct disposal of the crude glycerin prodeuced during the biodiesel production catalysed by homogeneous catalyst is not ethical due to its toxicity. Recovery of the glycerine after the transesterification can earn extra profit. Glycerine can be used as antifreeze agent and also as plasticiser. Therefore using solid catalyst, the recovery can be done by filter it using filtration method. The homogeneous catalyst otherwise are making the separation and liquid form of catalyst become difficult. The separation is costly and time consuming.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel

Biodiesel is an alternative choice of fuel for diesel engine. It is a renewable energy which is biodegradable, environment friendly and nontoxic. Using biodiesel can reduce the admission carbon dioxide from fossil fuel. The sources of biodiesel usually are vegetable oil and animal fat. The natural feedstock contains free fatty acid (FFA), phospholipids, water, odourants and other impurities (Meher, 2006).Major component in the feedstock are triglyceride which is a molecule of glycerol and 3 long chain carboxyl esters vary from C12 to C18. The different feedstock consist of different long chain carboxyl esters.

Recently government has the initiative to include the biodiesel in the fuel market. By blending the diesel fuel available with biodiesel to reduce the burden of consumption of diesel fuel alone. The future expected diesel fuel will be sold in the form of 5 percent biodiesel in mixture of diesel fuel in the market.As a result, biodiesel production is of interest of the world to reduce the consumption of diesel fuel in Malaysia that has created the global warming issues. (Siriwardhana, 2009)

2.2 Method of production of biodiesel

The few methods of biodiesel production are shown in Table 2.1 (Boro, 2012). After the comparison in the Table 2.1, Transesterification was chosen due to its flexibility and advantages.

Table 2.1 Methods of producing biodiesel, advantages and disadvantages.

Methods	Definition	Advantages	Disadvantages
Pyrolysis or thermal cracking	Method of conversion of one substance into desired products by application of heat with the aid of the catalyst in the absence of air or oxygen.	Low of processing costs, compatibility with infrastructure, engines and fuel standards, and flexible in choices of feed stock. The final products are identical to diesel fuel in composition.	High energy intensive.

Table 2.1 Continued

Methods	Definition	Advantages	Disadvantages
Micro-emulsions	Microemulsification uses vegetable oil mixed with alcohol and surfactant. The products can be blended with conventional diesel. The viscosity of the products was reduced to acceptable level.	Fuel viscosity is lower.Improve spray characteristics by explosive vaporization (flashing point） of the low boiling constituents in the micelles.	Lower cetane number and lower energy content.
Direct use and blending	Use vegetable oil directly orblend it with petrodiesel.	Liquid nature and portability Heat content (80% of diesel fuel) readily available; renewability	Higher viscosity, Lower volatility and occurring of reactivity of unsaturated hydrocarbon chains
Transesterification	Transesterifcation (also called alcoholysis) is the reaction of a fat or oil with an alcohol to form esters(FAME) and glycerine.	Renewability, with higher cetane number, lower emissions and higher combustion efficiency	Glycerol disposal and waste water problem.

2.3 Source of natural oil

Vegetable oil separated into edible oil and inedible oil. Edible oils are palm oil, sunflower oil, soybean and rapeseed oil. Inedible oil is either contains poisons or spent oil. The inedible oil such as jatropha oil is potential to be produced as biofuel (Endalew, 2011). Table 2.2.shows some elements contain in the oil.

Table 2.2 Carboxyl compositions and level of unsaturation in different feedstock.

FAME name	Chemical formula*	Soybean	Jatropha	Sunflower	Rapeseed	Pongamia	Palm
Lauric	12:0	-		-	-	-	0.1
Myristic	14:0	-	0-0.1	-	-	-	1
Palmitic	14:0	11	14-15.3	6.08	3.49	11.65	42.8
Palmmitoleic	16:0	-	0-1.3	-	-	-	-
Stearic	18:0	4	3.7-9.8	3.26	0.85	7.5	4.5
Oleic	18:1	23	45.8	16.93	64.4	51.59	40.5
Linoleic	18:2	54	44.2	73.73	22.3	16.64	10.1
Linolenic	18:3	8	0-0.3	-	8.23	-	0.2
Arachidic	20:0	-	0-0.3	-	-	-	-
Behenic	20:1	-	0-0.2	-	-	-	-

Source: (Endalew, 2011)

However, selection of catalyst is depending on the concentration of FFA in the oil. Table 2.3 shows the acid value containing in the vegetable oil. Endalew (2011) told that high value of FFA contains will favor the formation of Ca soap via saponification reaction when CaO used as catalyst. High concentration of FFA can be treated via neutralization or esterification using sulfuric acid (Kouzu, 2008).

Table 2.3 Properties of different feedstock.

Type of oil	Density, (g/cm^3)	Flash point, ^0C	Acid value (mg KOH/g)
Soybean	0.91	254	0.2
Rapseed	0.91	246	2.92
Sunflower	0.92	274	0.15
Palm	0.92	267	0.1
Peanut	0.9	271	3
Corn	0.91	277	0.11
JatropaCurcas	0.92	225	28
Palanga	0.9	221	44
Sea Mango	0.92	-	20

Source: (Endalew, 2011)

2.3.1 Potential of palm oil as raw material for biodiesel production

In Malaysia, the palm oil is utilized in food industry. However, palm oil has a high potential to be produced as biodiesel and in future to replace the conventional diesel. As Malaysia is the world 2nd largest palm oil producer,(Sceptregrouplimited, 2010) and palm oil has the potential to replace the rapeseed oil in producing biodiesel in the Europe country. Table 2.4 shows the properties of palm oil.

Table 2.4 Properties of Palm Oil

Properties	Value
Kinetic viscosity (38^{0}C)	39.6
Cetane number	42.0
Cloud point(^{0}C)	31
Flash point(^{0}C)	267
Density(kg/m^3)	918

2.4 Catalysts

2.4.1 Homogeneous catalysts

In the homogeneous base-catalyzed transesterification (Helwani, 2009) reported that alkaline metal alkoxides (combination of alkaline with alcohol), hydroxide, carbonates shown high performance in production of biodiesel. The by product can be recovered but formation of acetaldehyde and formaldehyde is occur because of overheated in recovery process. The most common basic catalyst NaOH (Zhang, 2010) residue in glycerine need large amount of water to wash the mixture of biodiosel. This process is not environmental friendly and glyceride discarded as waste causes environmental issues. In the acid-catalyzed reaction is much slower than alkaline reaction by 4000 times. Unlike base catalyst the triglycerides is protonated by acid catalyst to create tetrahedral intermediate. Therefore the two different homogeneous catalysts to be discernible and to proceed through different reaction rates (Endalew, 2011). However acidic catalysts are better in taking place of esterification of FFA. An example of acidic homogeneous catalyst is H_2SO_4.

Condition of acidic transesterification of acidic catalyst required high temperature as to speed up the reaction.

2.4.2 Heterogeneous catalysts

Heterogeneous system is different from homogeneous catalyst system. Endelew (2011) and Fogler (2006) stated that heterogeneous system consists catalysis, adsorption and desorption of reactant and product on the surface. Besides that, mass transfer phenomenon occurs during the catalytic reaction. These are the important parameter that used to calculate the rate of reaction. Findings are vital to study the important parameter to optimize the production.

In solid acid catalyst system, the absorbing element is the triglyceride on the surface of the catalyst but alcohol will react with the triglyceride absorbed on the surface of catalyst. The mechanism is based on the lewis /bronsted solid acid. The situation is same as solid base catalyst but alcohol will be absorbed on the surface and triglyceride will react with the absorbed alcohol. Few mechanism were studied such as, Langmuir-Hinshelwood (LH) and Eley- Rideal(ER) kinetic model.

Heteropoly acid as one of the solid acidic catalyst reviewed by Helwani (2011) perfectly synthesized biodiesel in short time. One of the examples is $Cs_{2.5}PW$. This catalyst can function under presence of water. It is so efficient that can produce 99% of biodiesel and not much affected by the appearance of FFA. Another type of solid acidic catalyst is the commercial type acidic resin catalyst, named Amberlyst15. Amberlyst may consider as efficient in both transesterification and esterification.

However, thermal-stability has to be overcome during operation under high temperature. (Lopez, 2008) & (Tesser, 2010)

Basic-porous supported catalyst such as alkaline metal oxide/zeolite having large surface area that provides high active site for the reaction to occur. This type catalyst can be prepared via impregnation method. Example ETS-10 containing lithium ions that is new generation in transesterification. Recently few solid form catalysts such as $CaTiO_3$, $CaMnO_3$, and alumina/silica supported K_2CO_3 is reported by Boro, (2012). Although the catalyst can be reused but the preparation method of these catalysts is not environmental friendly. Some abandoned waste like eggshell and oysters shell contains 95 percent of calcium carbonates and can be generated it into calcium oxide as catalyst. This catalyst can be generated again by calcinations. Yoosuk, (2010) revealed advance methods, such as hydration method. This method is to increase the surface area per gram of catalyst. CaO will react with water in the reflux system in 60 degree Celsius. Calcium oxide then transform to calcium hydroxide. Second step is to calcine the sample from first step in 600 degree celcius and calcium form again but with more porous than the untreated calcium oxide. The comparison and summary of homogeneous and heterogeneous catalyst is shown in Table 2.5.

Table 2.5 Comparison of the advantages and disadvantages for the different type of catalysts.

Type	Advantages	Disadvantages
Homogeneous	*Operate at ambient conditions. *Base catalysts give favorable kinetic. Since it's high activity and give high yield in short time *Basic catalysts are 4000 times faster reaction than acid catalyzed transesterification *Basic methoxides are more effective than hydroxides *Acid catalysts can be used for both esterification and transesterification simultaneously *Acid catalysts are suitable for low grade of feedstock and high contains of FFA	*Separation and waste problems after reaction *Catalyst impossible to be reused *Limited to batch type of reactors *Basic catalysts are sensitive to the presence ofFFA and water *Higher production cost compared with heterogeneous catalyst *Acid catalysts are corrosive, give very slow reaction rate and operate under high temperature. *Acid catalysts require higher molar ratio of methanol to oil, higher temperature, concentrated acid and more waste from neutralization reaction